CERTIFICATE OF MAILING BY FIRST CLASS MAIL (37 CFR 1.8)	Docket No.
Applicant(s): Yasushi AKIYAMA et al.	2002JP311

Serial No. 10/519,242	Filing Date December 22, 2004	Examiner WU, Ives J.	Group Art Unit 1713

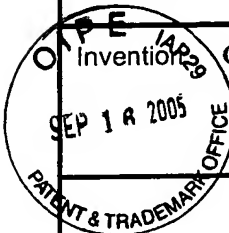Invention: COMPOSITION FOR ANTIREFLECTIVE COATING AND METHOD FOR FORMING SAME

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Chemical Amplification in the Design of Dry Developing Resist Materials

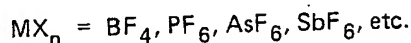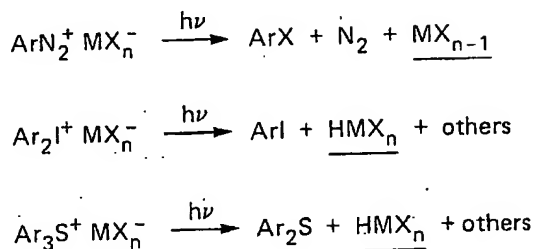HIROSHI ITO *and* C. GRANT WILLSON

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A new resist system is described which undergoes spontaneous relief image formation. The resist is formulated from end capped poly(phthalaldehyde), PPA, and a cationic photoinitiator such as a diaryliodonium or triarylsulfonium metal halide. The extreme sensitivity of the resist is the result of designing for chemical amplification. The desired amplification results from the fact that photolysis of the sensitizer generates acid which catalyzes main chain cleavage of the polyaldehyde. The uncapped polymer is thermodynamically unstable with respect to reversion to monomer at room temperature so a single acid catalyzed scission results in complete depolymerization to volatile monomer. A single radiochemical event is thereby amplified in the sense that it produces an enormous number of subsequent chemical transformations. PPA/onium salt resist films are so sensitive that exposure to low doses of e-beam, X-ray or ultraviolet radiation results in complete self development without post-exposure processing of any kind. The exposed area simply vaporizes.

INTRODUCTION

The function of the classical diazoquinone/novolac resists is based on a radiation induced structural transformation of the diazoquinone sensitizer which produces a large change in its efficiency as a dissolution inhibitor. The efficiency of the crucial photochemical transformation is characterized by the quantum yield for the process expressed as molecules transformed per photons absorbed. The quantum yield of typical diazoquinones is 0.2 to 0.3. Thus, three or four photons are required to transform a single molecule of sensitizer. This places a fundamental limit on the photosensitivity of such systems. In order to circumvent this intrinsic sensitivity limitation we have sought to design resist material systems that incorporate chemical amplification of the sort that characterizes the silver halide photographic emulsion systems. In these systems a single photo event initiates a cascade of subsequent chemical reactions that ultimately express the intended function.

Amplification of this sort is observed in several negative resist systems. One example of such a system involves the use of cationic photoinitiators in epoxy resins (1-6). Most of this work is based on the use of aryldiazonium salts, diaryliodonium salts or triarylsulfonium salts which generate strong acids upon exposure (*Scheme 1*). These acids initiate the cationic, ring opening polymerization of the oxirane residues that ultimately results in crosslinking. Here amplification is achieved by the catalytic nature of the initiation process. The acid is not consumed in the initiation step and can function to initiate several chains. Very sensitive negative resists have been developed that function on this basis (7).

$$ArN_2^+ \, MX_n^- \xrightarrow{h\nu} ArX + N_2 + \underline{MX_{n-1}}$$

$$Ar_2I^+ \, MX_n^- \xrightarrow{h\nu} ArI + \underline{HMX_n} + \text{others}$$

$$Ar_3S^+ \, MX_n^- \xrightarrow{h\nu} Ar_2S + \underline{HMX_n} + \text{others}$$

$$MX_n = BF_4, PF_6, AsF_6, SbF_6, \text{etc.}$$

Scheme 1. Photochemistry of onium salts.

We have explored the sensitized epoxy design in our laboratory. This work is exemplified by successful imaging of thick (6μ) films of Epi-Rez SU-8 epoxy resin (Celanese) by sensitizing the resin with *p*-hexyloxybenzenediazonium hexafluorophosphate. *Figure 1* shows high resolution negative images generated in such a formulation by exposure to 313 nanometers (nm) light and subsequent development in a nonpolar solvent.

We have recently focused our attention on the design of positive tone resist systems that incorporate chemical amplification. One such new class of positive resist materials is based on photochemical generation of a substance that catalyzes the cleavage of pendant groups on the side chains of appropriately functionalized polymers. Here, the effective quantum efficiency of the
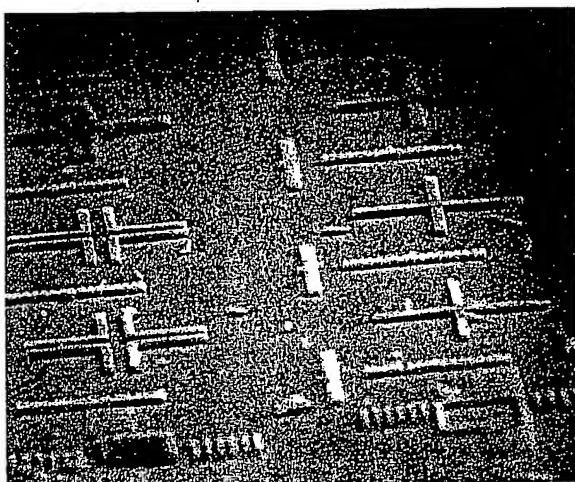
Fig. 1. *Negative tone images printed in Celanese Epi-Rez SU-8 epoxy resin sensitized with n-hexyloxybenzenediazonium hexafluorophosphate exposed at 313 nm.*

Fig. 2. *PBOCST sensitized with diphenyliodonium hexafluoroarsenate and exposed at 254 nm. The image on the left is positive tone developed with MF312-water (1:1) and the image on the right is negative tone developed with CH_2Cl_2-hexane (2:1).*

Fig. 3. *Thermogravimetric analysis of polyphthalaldehyde synthesized by butyllithium initiation and end capped by acylation.*

system is the product of the quantum yield of the photochemical event and the number of side chain transformations achieved by one molecule of the catalyst. This multiplicative response constitutes gain of the sort we seek.

A polymer upon which the new system is based is poly(*t*-BOC-*p*-hydroxystyrene), PBOCST. We have synthesized PBOCST both by chemical modification of commercially available poly(*p*-hydroxystyrene), Maruzen oil, and by radical polymerization of the appropriately substituted styrene monomer. The sensitizers for this system are again, various onium salts that undergo efficient photolysis to produce strong acids. Among the salts tested to date, triphenylsulfonium hexafluoroarsenate and diphenyliodonium hexafluoroarsenate are particularly effective.

The system functions, mechanistically, in the following way. Photolysis of the salts generates a local concentration of strong Bronsted acids. Upon post-exposure baking (100°) for a few seconds, the BOC group undergoes acidolysis to produce two volatile products, carbon dioxide and isobutylene, and liberate the phenolic hydroxyl. The resulting change in the polarity and solubility characteristics of the polymer is very large. Hence, the exposed areas can be selectively dissolved in polar solvents to provide positive tone images of the mask. Furthermore, if the developing solvent is nonpolar, the unexposed areas can be selectively dissolved to leave a negative tone image of the mask.

We have succeeded in producing excellent high resolution images in the new PBOCST resist (*Fig. 2*). It is very sensitive to deep UV radiation and can be dye sensitized for exposure in the mid UV or at conventional wavelengths. The materials are also sensitive to *e*-beam exposure (8).

We have now succeeded in designing a second stage of amplification into a positive resist material. In the conceptual design, one stage of amplification is achieved by choosing polymers which, when subjected to a single scission reaction, undergo spontaneous
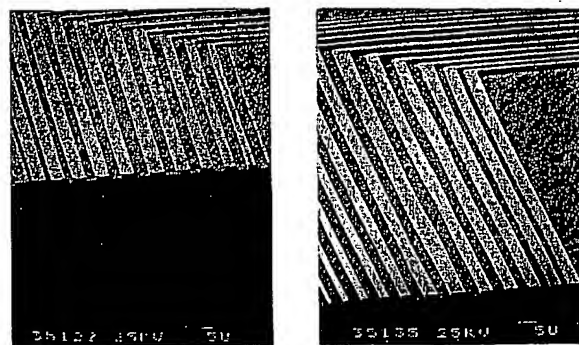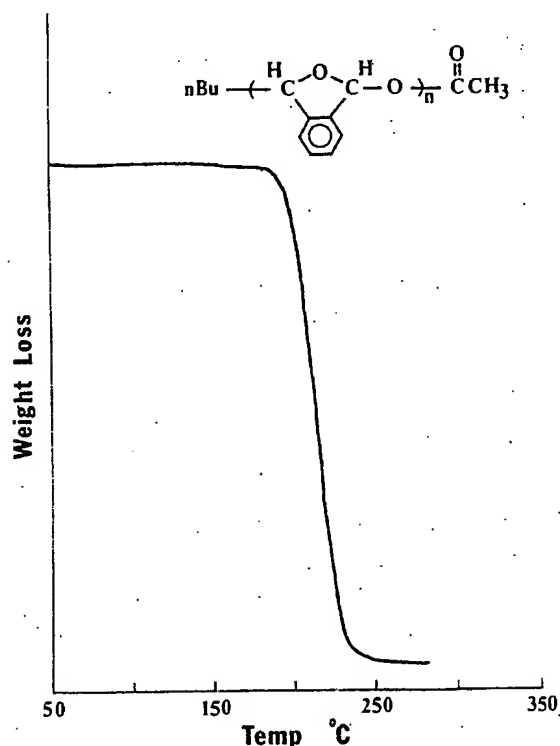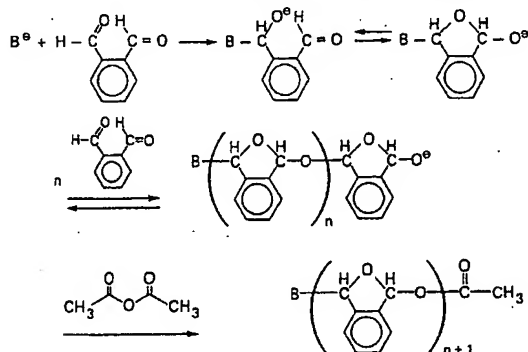
depolymerization that results in complete reversion to monomer. The second stage of amplification is achieved by including a substance which undergoes radiolysis to produce a product that catalyzes scission of the unstable polymer.

The polymer upon which the new system is based is a polyaldehyde. Aldehydes undergo anionic or cationic polymerization in a reversible, equilibrium reaction. Many of these systems have ceiling temperatures well below room temperature such that the polymerizations must be run at cryogenic temperatures and if the polymer is isolated, it rapidly depolymerizes to monomer. If, however, these polymers are end capped by acylation or alkylation prior to isolation and warming, they are of-

ten quite stable. Vogl, *et al.* have extensively and intensively studied the equilibrium polymerization of aliphatic aldehydes (9). Most of these materials are intractable, insoluble substances because of their high crystallinity. Certain aromatic dialdehydes such as phthalaldehyde and o-formylphenylacetaldehyde (10) undergo cyclopolymerization with a ceiling temperature of approximately −40° (*Scheme 2*). These aromatic materials after end capping, are stable to greater than 150° as evidenced in the thermogram presented as *Fig. 3* and unlike their aliphatic counterparts, are soluble in common organic solvents. We have found poly(phthalaldehyde) to be particularly useful for our systems.

We are not the first to explore the utility of poly(aldehydes) as imaging media. Solvent development of e-beam exposed PPA has been reported (11). Aliphatic polyacetals with photosensitive end groups have also been studied but suffer from low sensitivity as does an invention describing a photoimaging system in which the aldehyde monomer released from a poly(acetal) upon radiation followed by heating is used to crosslink certain polyamides (12). Sensitization of PPA by addition of substances which release acids upon radiolysis such as poly(vinyl chloride) or phenol derivatives has also been applied to an imaging technology based on changes in optical density (13), and as resist materials wherein images were obtained by heating and/or solvent development after exposure (14). We have found that high molecular weight PPA, sensitized by addition of cationic photoinitiators is so sensitive that it undergoes clean, spontaneous relief image formation (self development) upon exposure to very low doses of e-beam, X-ray or ultraviolet radiation.

Dry developing resist materials have been sought for some time (15-17). The interest in such materials throughout the semiconductor industry stems from the potential they provide for higher throughput and higher yields. The higher yields result from both a reduction in process steps and the fact that such materials provide the potential for carrying our exposure, development, and pattern transfer under high vacuum, thereby reducing defects due to atmospheric contaminants and the development process. Dry processed X-ray negative resists that require plasma or RIE steps after exposure have been reported (16). Polymethacrylonitrile has been shown to dry develop upon heating after electron

beam exposure (17). However, plasma etching is required to completely develop the images. Self development of certain poly(olefin sulfones) has also been reported (15), but complete development to substrate can be achieved only with very thin films under relatively high dose electron beam exposure conditions with simultaneous heating above 90°C. The PPA/onium salt system is the only resist of which we are aware that undergoes clean self development without the need for post-exposure processing of any kind.

RESULTS AND DISCUSSION

Our attempts to measure the γ-ray G value of end capped polyphthalaldehyde produced interesting results. When irradiated PPA samples were subjected to GPC (gel permeation chromatographic) analysis as received, no polymer peaks were detected even though the tubes of irradiated polymer contained solid material. However, when irradiated samples were subjected to an end capping reaction prior to analysis, normal chromatograms were observed (*Fig. 4*). *Figure 5* indicates that PPA reverts to monomer upon exposure to γ-radiation to an extent that is dependent on dose. We believe that at 6 Megarads (Mrad) virtually every chain has been scissioned but must conclude complete

Fig. 4. Gel permeation chromatograms of γ-radiolyzed PPA. The trace on the left obtained by analysis after exposure. The trace on the right was obtained from samples that were reacylated after exposure.

Fig. 5. Molecular weight and polymer yield of PPA exposed to γ-radiation and then reacylated after exposure.

Scheme 2. Anionic polymerization and end capping of polyphthalaldehyde.

unzipping occurs rapidly only when the scissioned polymer is dissolved.

Exposure of unsensitized PPA films to *e*-beam exposure followed by baking above 100° provides high resolution relief images at 5 to 20 microCoulomb (μC)/per square centimeter (cm^2). However, the images are very shallow. Exposure to UV radiation results in approximately 15 percent loss in film thickness after heating. The UV imaging process is oxygen dependent. It does not occur when films are exposed *in vacuo*.

We reasoned that in order for the depolymerization to occur efficiently, a rational cleavage (scissioning) mechanism must be provided that generates a chain end that is a hemiacetal or hemiacetal ion in order to reestablish the polymerization equilibrium. Simple nonspecific cleavage to radical species should not be expected to produce the desired result. Consequently, we prepared copolymers of phthalaldehyde and *o*-nitrobenzaldehyde in attempt to increase the efficiency of the initial photo event. Exposure of copolymer films containing about 3 percent of *o*-nitrobenzaldehyde units to UV radiation resulted in relief image formation upon post-baking, with up to 60 percent loss in the film thickness in the exposed regions. We have found that photo-fragmentation did occur at the *o*-nitrobenzaldehyde acetal linkages as expected (18) (*Scheme 3, Fig. 6*). Fragmentation produced one hemiacetal chain end which depolymerized but the other photo fragment was shown to be terminated by an *o*-nitrosobenzoate linkage and therefore, efficiently capped (*Scheme 3*), as evidenced by the model reaction study (*Fig. 7*).

We next turned to sensitization of polyphthalaldehyde through incorporation of substances that produce strong Lewis or Bronsted acids upon radiolysis (*Scheme 1*) (1-6) in hope of achieving catalytic acidolysis of the acid-labile main chain acetal linkages (*Scheme 4*). Addition of certain cationic photoinitiators produced a dramatic result. For example, addition of triphenylsulfonium or diphenyliodonium metal halides (10 weight percent to the polymer) has allowed imaging of 1μ thick
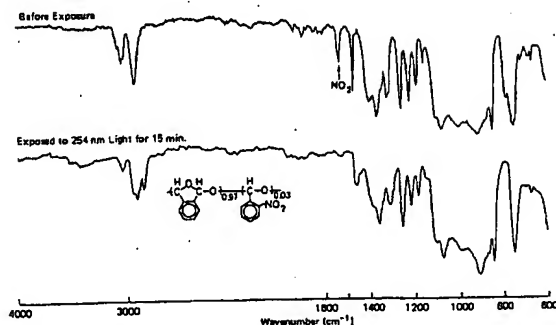
Fig. 6. *Infrared spectra of poly(phthalaldehyde-co-2-nitrobenzaldehyde) before and after exposure to 254 nm light. Note the disappearance of the NO$_2$ absorption.*
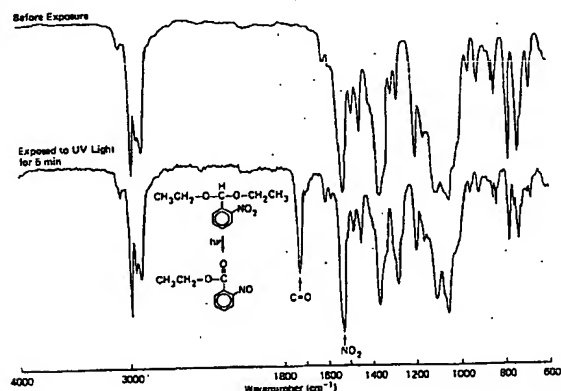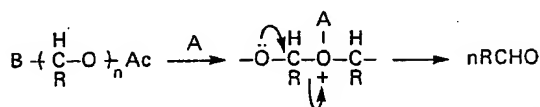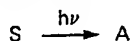
Fig. 7. *Infrared spectra of the model compound 2-nitrobenzaldehyde diethylacetal before and after exposure to 254 nm light. Note the generation of the nitrosoester carbonyl absorption.*

Scheme 4. *Chemical amplification by sensitization with onium salts.*

films of polyphthalaldehyde at 2 to 5 millijoule (mJ)/cm^2 of deep UV radiation and at 1.0 μC/cm^2 of 20 keV electron beam radiation: Clean relief patterns with resolution below 1μ line width are generated by exposure alone even without heating.

In a typical experiment, polyphthalaldehyde was dissolved in diglyme or cyclohexanone at 20 w/v% of solids, to which was added triphenylsulfonium or diphenyliodonium hexafluoroarsenate at 10 w/w% to the polymer. Films were spin-cast on silicon wafers, baked at 100°C for 10 minutes, and exposed. Optical micrographs of the resist images generated upon X-ray electron beam, and UV exposure are shown in *Figs. 8, 9, and 10*, respectively.

The UV sensitivity of the system depends on the loading and structure of the onium salt. For example, at 10 weight percent loading, the sensitivity with triphenylsulfonium hexafluoroarsenate (1.5 to 5 mJ/cm^2), diphenyliodonium hexafluoroarsenate (5 mJ/cm^2), and
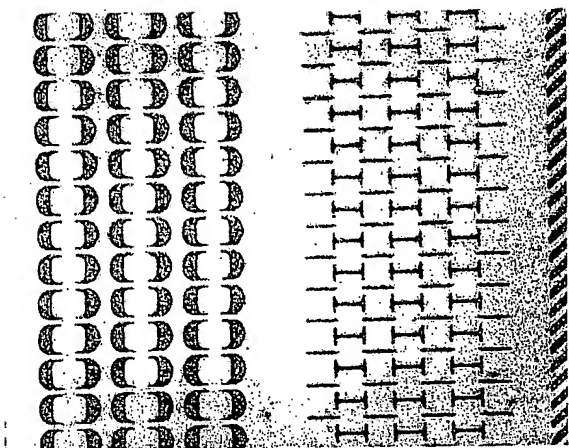
Scheme 3. *Photosensitization of PPA by copolymerization with 2-nitrobenzaldehyde.*

Fig. 8. *Self developed PPA resist sensitized with diphenyliodonium hexafluoroarsenate exposed to Al-K$_\alpha$ X-ray radiation. Minimum feature is 1.0μ.*
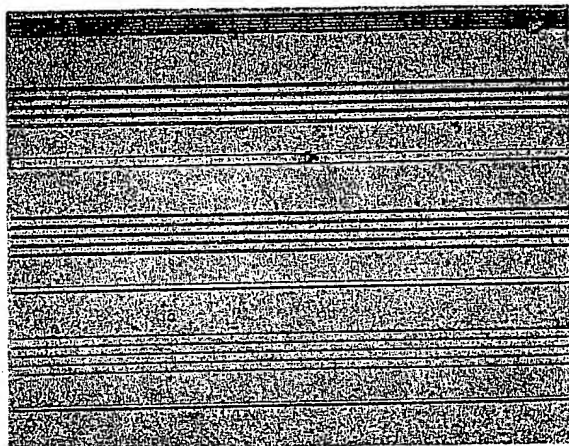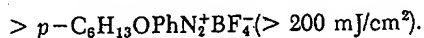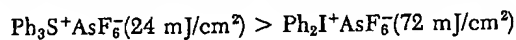

Fig. 9. *Self developed PPA resist sensitized with diphenyliodonium hexafluoroarsenate exposed to 1 μC/cm² of 20 keV electron beam radiation. Minimum written feature is 0.25μ.*

Fig. 10. *Self developed PPA resist sensitized with triphenylsulfonium hexafluoroarsenate exposed to 2.4 mJ/cm² of deep UV (254 nm) radiation. Minimum feature is 0.7μ.*

Fig. 11. *Infrared spectra of PPA resist cast on sodium chloride before exposure, after very low dose exposure and after heating. Note generation of an intense aldehyde carbonyl due to monomer.*

p-hexyloxybenzenediazonium tetrafluoroborate (6.5 mJ/cm²) is similar, but at 2 weight percent loading a much higher dosage is required to achieve self development and the order of the sensitivity is as follows:

$$Ph_3S^+AsF_6^-(24 \text{ mJ/cm}^2) > Ph_2I^+AsF_6^-(72 \text{ mJ/cm}^2)$$

$$> p-C_6H_{13}OPhN_2^+BF_4^-(> 200 \text{ mJ/cm}^2).$$

In any case, formation of monomeric phthalaldehyde due to acidolysis and depolymerization is clearly demonstrable by IR spectroscopy (*Fig. 11*).

Attempts to obtain scanning electron micrographs of PPA resist images has not been successful. The unexposed resist rapidly vaporizes in the microscope. We were surprised, therefore, to discover that electron beam generated relief images in PPA can be transferred into SiO₂ by either CF₄/O₂ plasma etching (*Figs. 12*, and *13*) or by treatment with buffered HF.

One might expect that resist systems as sensitive as PPA and, in particular, resist systems that incorporate catalytic species and chemical amplification might have very limited resolution. In theroy, a single acid
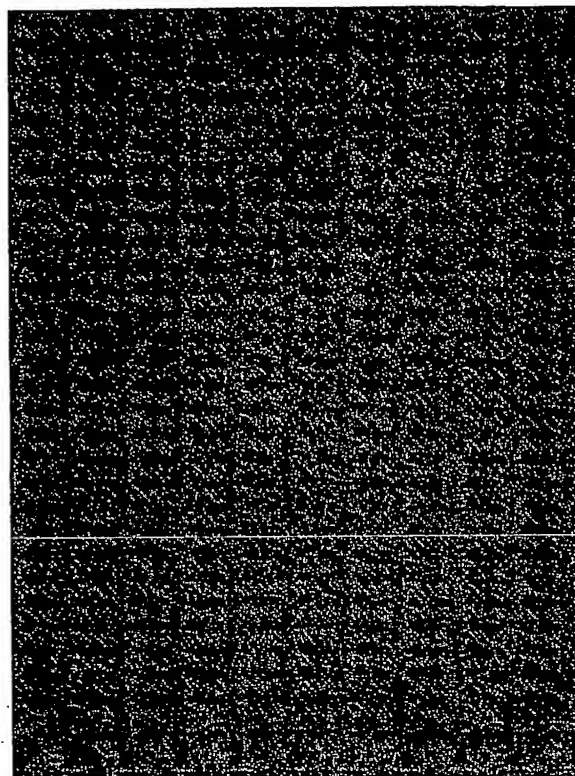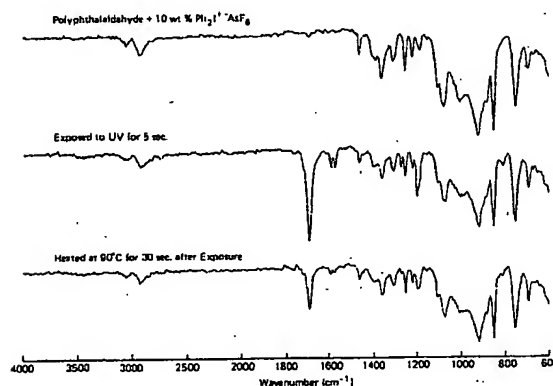
generating photo event should be sufficient to crosslink an entire film of epoxy resin or to depolymerize an entire PPA film. Fortunately, this is not observed experimentally as evidenced by the submicron images presented in the accompanying micrographs. Either the diffusion lengths of the acid catalytic species are very short in the glassy matrix or there exist a sufficient number of available terminating reactions to limit the lateral extent of the reactions in a film.
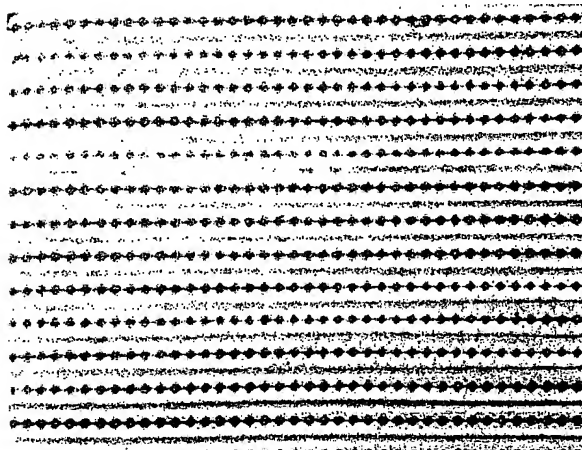
Fig. 12. Self developed patterns in 1 μC/cm² e-beam exposed PPA resist on SiO₂.

We are continuing to explore the limits of the PPA resist as well as other systems that incorporate chemical amplification.

EXPERIMENTAL

Phthalaldehyde purchased from Aldrich Company was purified by recrystallization from CH_2Cl_2-hexane, and polymerized by anionic initiation with n-butyllithium, phenylmagnesium bromide, or potassium t-butoxide/18-crown-6 as initiator in tetrahydrofuran at −78°C under high vacuum with use of a break-seal technique. All of the polymerizations were terminated by adding a cold mixture of acetic anhydride and pyridine at −78°C to end-cap the polymer. As shown in *Table 1*, the end-capped polymers are of high molecular weight, stable to about 180°C according to TGA analysis, soluble in common organic solvents, and can be spin-cast from solution to provide clear, isotropic, noncrystalline films.

^{60}Co γ-radiation of the polymer powder was performed by The National Bureau of Standards (Washington, D. C.). The polymer powder was sealed in a glass tube under high vacuum and exposed at room temperature. Electron beam exposures were carried out with an IBM Vector Scan e-beam Exposure Tool at 20 keV. X-ray exposures were carried out under vacuum by Al-K_α radiation, and UV exposures with Cannon PLA or Oriel illuminator in the contact mode.

IR spectra were recorded on a Perkin-Elmer 283 spectrometer and UV spectra on a Hewlett Packard 8450A UV/VIS spectrophotometer. Molecular weight determinations by GPC were made using a Waters Model 150 chromatograph equipped with six or eight
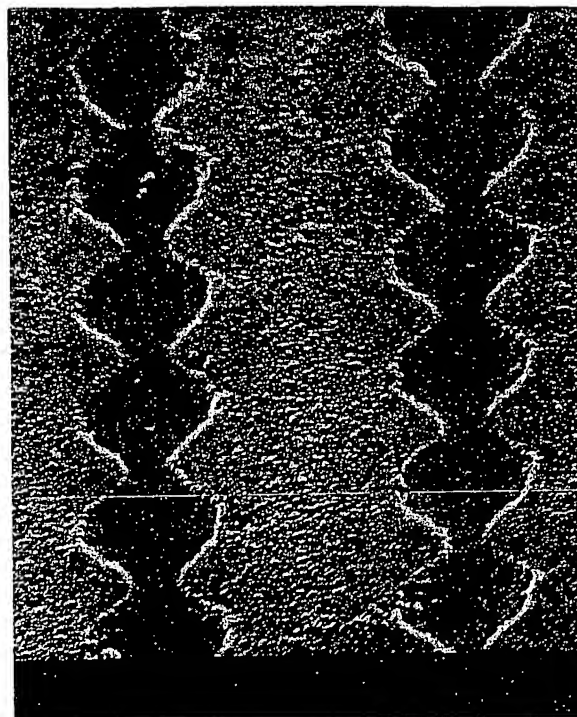

Fig. 13. CF₄ plasma etched image transfer of resist pattern shown in Fig. 12. SiO₂ thickness is 1000 Angstroms.

microstyragel columns at 30 or 40°C in tetrahydrofuran. TGA measurements were performed on a DuPont 951 at a heating rate of 10°C/min.

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Table 1. Anionic Polymerization of Phthalaldehyde in THF at −78°C

Polymn. No.	Initiator (mole %)	Time hr	Yield %	Mn × 10^{-3}	Mw × 10^{-3}	D
30	PhMgBr (0.65)	22	89.5	54.3	97.1	1.79
33	nBuLi (0.33)	49	94.6	34.8	54.9	1.58
37	KOBu'/18-crown-6 (0.16)	72	78.9	30.8	98.5	3.20
64	nBuLi (1.18)	72	89.4	11.0	16.8	1.53
67	nBuLi (0.58)	72	90.5	36.9	43.0	1.17

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